Rel. to corresp. to GB 1,442,858

PATENT SPECIFICATION

NO DRAWINGS

1,050,836

1,050,836

Date of Application and filing Complete Specification: July 26, 1965.

No. 31688/65.

Application made in United States of America (No. 388304) on Aug. 7, 1964.

Complete Specification Published: Dec. 7, 1966.

Index at acceptance:—D1 P(AX, B2A2, B2B1, B5A, C2A9, C2A12A3, C2A12A5, C2A12A6, C2A12AX, C2A12B1, C2A12B3, C2A12B4, C2A12B5, C2C2, C2C3, C2C9, C2C11); C3 P(2C8C, 2C11, 2C13A, 2C17, 2C20B, 2D1A, 2K7, 2K8, 2T2A); C3 Q(C8C, C11, C13A, C17, C20B, D1A, T2A)

Int. Cl.:—D 06 m//C 08 c, d

COMPLETE SPECIFICATION

Adhering Textile Materials to Rubber

We UNITED STATES RUBBER COMPANY, of Rockefeller Centre, 1230 Avenue of the Americas, New York 100-20,, State of New York, United States of America, a corporation organized and existing under the laws of the State of New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improvements in the method of adhering textile materials to rubber, and to the improved laminates so obtained.

In certain rubber articles designed to withstand considerable stresses in use, the rubber is reinforced with plies of comparatively inextensible textile materials. Thus, rubber hose, belts and tires are commonly reinforced with filamentary textiles in the form of yarns, cords or fabric. In such articles, it is important that the plies of textile reinforcing material be firmly adhered to the rubber intermediate the textile plies and remain effectively adhered even after the article has been subjected to repeated varying strains in use, because any separation and relative movement of the rubber and textile parts leads to abrasion between these parts and consequent failure. In order to improve the adhesion of the textile material to the rubber intermediate the textile plies, it is common practice to first apply a deposit of rubber on the textile material, such as a tire cord fabric, by passing the textile material through a bath of an aqueous dispersion of rubber, such as a rubber latex composition, as in a so-called "solutioning" treatment, and drying. The rubber latex "solutioning" composition preferably contains a resin, e.g. a fusible partially reacted resorcinol-formaldehyde resin, such as a condensate of resorcinol and formaldehyde in the ratio of 1 mole resorcinol to 0.5 to 0.8 mole of formaldehyde, and formadehyde or a formaldehyde-yielding agent which on subsequent heating as during vulcanization of the rubber intermediate the textile plies cures the fusible resin to an infusible state.

According to one aspect of the present invention, a laminate comprises a textile material and a vulcanized rubber composition, the rubber composition containing the *in situ* formed reaction product of N,N′-dimethylol urea with resorcinol or a condensation product of resorcinol with acetone or a partially reacted condensation product of resorcinol with formaldehyde or acetaldehyde. A method of making such a laminate comprises incorporating the N,N′-dimethylol urea and the resorcinol or condensation product into a heat-vulcanizable rubber composition, applying the composition to the textile, and heating the assembly so as to form the reaction product and vulcanise the rubber. The invention leads to a further improvement in adhesion of the textile material to the rubber intermediate the textile plies in addition to that obtained by the latex "solutioning" treatment of the textile material.

Fusible partially reacted resorcinol-formaldehyde resins used in the invention, and those used in the above-mentioned latex "solutioning" compositions, may be prepared in known manner by heating a concentrated aqueous solution of the resorcinol and formaldehyde, with or without a catalyst such as oxalic acid. The resorcinol and acetaldehyde are readily condensed in an

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easily controlled reaction using an acid such as acetic, or hydrochloric acid as a catalyst in aqueous or alcohol medium on standing or by heating at temperatures up to reflux. The condensation products of resorcinol and acetaldehyde, which are tacky amber-like materials, are known. The resorcinol and acetone are readily condensed using dilute hydrochloric acid as a catalyst or standing at room temperature or by heating at temperatures up to reflux. The condensation products of resorcinol and acetone, which are white powders, are known. The N,N'-dimethylol urea is a known compound.

The rubber intermediate the textile plies may be applied in the usual manner by calendering a coating of a solid vulcanizable rubber composition containing the N,N'-dimethylol urea and the resorcinol or condensation product on the textile, generally on both sides, e.g. as in the conventional coating of tire cord fabric with tire carcass stock. The N,N'-dimethylol urea and the resorcinol or condensation product may be mixed with the conventional compounding ingredients in the solid rubber in a Banbury mixer and the rubber composition then calendered on the textile material. After building the rubber-coated textile material into the finished article, e.g. a tire, the assembly is heated to vulcanize the rubber and react the resin components of the invention. The ratio of the two components of the invention is not critical and generally will be from 0.3 to 3 parts by weight, preferably about one part, of the N,N'-dimethylol urea per part of the resorcinol or condensation product. The amount of these two components mixed with the rubber is not critical. Generally 1 to 10 parts by weight, and preferably 3 to 6 parts by weight, of the two components (total) per 100 parts of the rubber will be mixed in the rubber compound to be calendered on the textile material. Where the textile material is passed through a rubber latex "solutioning" bath and dried, the deposit on the thus treated textile material will be in the range of 2 to 15 percent, preferably 4 to 10 percent, of latex solids based on the weight of the textile material.

The solid rubber used in the present invention for making the rubber and fabric laminates for use in tire manufacture and for other purposes may be natural (Hevea) rubber or conjugated diolefine polymer synthetic rubber or mixtures of any of them including their reclaims. The aqueous dispersion of rubber, when used for "solutioning" the textile material before plying with the solid rubber composition, may be natural rubber latex, or a latex of conjugated diolefine polymer synthetic rubber, or mixtures thereof, or an aqueous dispersion of reclaim from such rubbers, or mixtures of any of such latices and reclaim dispersions. Such conjugated diolefine polymer synthetic rubbers are polymers of butadienes-1,3, e.g. butadiene-1,3, isoprene, 2,3-dimethyl-butadiene-1,3, and copolymers of mixtures thereof, and copolymers of mixtures of one or more such butadienes-1,3 with one or more other polymerizable compounds which are capable of forming rubbery copolymers with butadienes-1,3, for example, up to 60% by weight of such mixture of one or more monoethylenic compounds contain a $CH_2=C\diagup\diagdown$ group where at least one of the disconnected valencies is attached to an electro-negative group, that is, a group which substantially increases the electrical dissymmetry or polar character of the molecule. Examples of compounds which contain a $CH_2=C\diagup\diagdown$ group and are copolymerizable with butadiene-1,3 are aryl olefins, such as styrene, vinyl toluene, alpha methyl styrene, chlorostyrene, dichlorostyrene, vinyl naphthalene; the alpha methylene carboxylic acids and their esters, nitriles and amides, such as acrylic acid, methyl acrylate, methyl methacrylate, acrylonitrile, methacrylonitrile, methacrylamide; vinyl pyridines, such as 2-vinyl pyridine, 2-methyl -5- vinyl pyridine; methyl vinyl ketone. Examples of such conjugated diolefine polymer synthetic rubbers are polybutadiene, polyisoprene, butadiene-styrene copolymers (SBR) and butadiene-acrylonitrile copolymers. The rubber intermediate the plies will also contain conventional compounding and vulcanizing ingredients such as carbon black, rubber processing or softening oils which may be added as such or may be present from oil-extended rubbers, antioxidants, sulfur, zinc oxide and accelerators. The textile material may be any of the conventional textiles used for reinforcing rubber, such as native cellulose (e.g. cottons), regenerated cellulose (e.g. rayons) and synthetic linear polyamides or nylons (e.g. polycaprolactam or nylon 6 and polyhexamethylene-adipamide or nylon 66), and may comprise cords or woven fabrics.

The following examples illustrate the invention. All parts, ratios and percentages referred to herein are by weight. Examples 1 to 4 show the preparation of the N,N'-dimethylol urea, the partially reacted resorcinol-formaldehyde resin, the resorcinol-acetaldehyde condensate and the resorcinol-acetone condensate, respectively, used in Examples 5 and 6 which show the use of N,N'-dimethylol urea and resorcinol or condensation product for improving the adhesion of rubber to textile material.

EXAMPLE 1

To a solution of 1.9 parts of sodium acid